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Abstract

Progress has been made in characterizing the parameters needed to achieve selective electrodeposition onto a nanostructured surface and in techniques and procedures needed to create a nanoheterostructure, a class of composite solid-state/solid-state and biomolecular/solid-state materials with nanometer-scale structure. A newly created device called a minicell, a minielectrochemical cell, proved to be very successful in terms of dealing with the small substrate size (usually less than 20 mm²) on which our nanostructures are formed. We found that a properly designed electrochemical cell for these experiments should have the working-reference and working-counter electrode distances the same. It should also use a counter electrode with a large surface area exposed to the electrolyte, and one which is located over the whole working electrode, so that deposition occurs smoothly and uniformly across the entire substrate surface.

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FINAL REPORT for ARO Contract DAAL 03-92-G-0085, "Composite Nanostructured Material Fabrication by Electrochemical Scanning Probe Microscopy," for the period 3/01/92 through 8/31/92.

In this proposal we have begun to explore a means of accomplishing selective electrodeposition to fabricate a new class of composite solid-state/solid-state and biomolecular/solid-state materials with nanometer-scale structure called *nanoheterostructures*. As an example of such a structure we would start with a nanostructure consisting of a metal film of material A which has nanometer-scale periodic holes in it. We would then fill the holes with a different metal B resulting in a bimetallic material with nanometer-scale periodicity. An example of such a structure is given in Figure 2 in the research proposal.

Progress has been made in characterizing the parameters needed to achieve selective electrodeposition onto a nanostructured surface and in techniques and procedures needed to create a nanoheterostructure. The first attempts to characterize the type of surface present in our nanostructures employed a newly created device called a minicell which proved to be very successful in terms of dealing with the small substrate size (usually less than 20 mm²) on which our nanostructures are formed [1]. The cell utilizes a three electrode system (working, counter, and reference) in a spatial relationship that maximizes current flow and working-counter electrode potential difference measurements. The cell is set up so that our substrate serves as the working electrode, with an electrical contact made through the back of the substrate. A capillary tube is brought to the surface of the substrate, which is inverted so that the face of the substrate points down. The capillary tube is connected to a three-port "T" connector. Also attached to the connector is a thin tygon tube through which electrolyte solution is injected into the system. The third port of the connector contains the other two electrodes (counter and reference). A platinum 18 gauge needle, squared off at both ends, serves as the counter electrode. Threaded through the counter electrode is a piece of silica-lined HPLC tubing, and threaded through it is a 0.1mm platinum wire which serves as the quasi-reference electrode. The tip of the reference wire and the HPLC tubing are made flush with the end of the counter electrode, and the counter/reference electrodes are positioned about 3/4-1 inch away from the working electrode (substrate). The entire assembly is positioned close to the sample using an X-Y-Z micromanipulator and electrolyte is injected until a drop formed between the capillary tube and the sample. Electrochemistry can then be performed on the substrate surface.

A ferricyanide solution was used to characterize the substrate as an electrode and this solution was about 5 mM Fe(CN)₆³⁻, 1 M KCl, although other concentrations were tried. On bare HOPG, good current readings were obtained, and were typically on the order of 15 microamps for milled HOPG and 5 microamps for non-milled HOPG (experiments were done to show that the roughening of the surface created a better electrode). Other experiments performed using the minicell and the ferricyanide couple used metallized but unmilled S-layers on an HOPG substrate. In this configuration, no current flow was observed, which is what one would expect given that the conductive HOPG was covered with a non-conductive TiO_x layer. When metallized and milled S-layers were used with the minicell, small currents were seen, indicating

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that perhaps, just as is desired, only the HOPG exposed at the hole sites in the TiO_x overlayer created by milling were involved in an electrochemical process.

At this time, the electrochemical attachments to our atomic force microscope (ECAFM) were obtained. This included a three-electrode potentiostat which attached to the base of the microscope and a 4-port fluid cell used for imaging and simultaneously conducting electrochemical experiments. Our efforts then turned to using the fluid cell as an electrochemical cell. In order to test the fluid cell and potentiostat we attempted to perform the test experiments suggested by the manufacturer. This involved using an electrolyte composed of 0.05 M PbO in 0.1 M perchloric acid. A 0.5 mm Pt wire was used as the counter electrode, and was inserted into the hole in the top of the fluid cell intended for the counter electrode, and was bent over so that it ran parallel to the surface of the underlying substrate and was about 3 mm away. The reference electrode was a 1 mm Pb wire, which was initially inserted in the port intended for the reference electrode. The reference electrode was never closer than 5 mm from the sample. The other two ports on the fluid cell were used to bring in and let out the electrolyte. Using this set up, reproducible cyclic voltammograms (CV) were produced, but they did not resemble those which were obtained by the manufacturer. They typically showed no current flow when scanning the potentials in which the manufacturer got deposition, and showed large current flows (400-500 microamps) when larger potentials were attempted. Second, a stable resting potential was never obtained, which indicated that the Pb reference might be having problems in the solution.

We generally observed that we were having problems with leaks around the counter electrode, and that the lead electrode was very unstable. In order to solve these problems, we switched over to using the minicell again so that we could locate the deposition parameters for depositing lead from our solution onto HOPG without having to worry about leakage problems. Second, we switched to using a Pt counter and Pt reference electrode. In this arrangement, we used the Pt needle described above as the counter electrode and a 0.1 mm Pt wire for the reference electrode. The sample (substrate) onto which we were plating was electrically connected to the base of the ECAFM so that it would still serve as the working electrode. In this configuration, we observed current flows (about 20-70 microamps) that were reasonable, and obtained without ramping the potential too far from the resting potential. When the HOPG that had been used with this cell was imaged in air, large islands of lead were observed. Thus, the first successful deposition experiment onto a bare substrate was done using the minicell.

Because we had had good luck with the counter/reference assembly used in the minicell, we decided to use it in conjunction with the fluid cell. To do this, two ports of the fluid cell were blocked (the two intended for the counter and reference electrodes, respectively). As for the other two ports, one was used to inject electrolyte into the cell, and the other was used both as the port from which the solution exited the cell, and as the port in which the minicell's counter/reference assembly was inserted. Because this configuration put the reference electrode very near the counter electrode (and thus, the working-reference and working-counter electrode distances were almost identical), very good looking CV's were generated and showed the processes of plating and deplating lead from an HOPG surface. The other factor that was maximized in this configuration was the size of the counter electrode. The surface area of the platinum needle was about as large as the surface area of the working electrode (substrate). Thus, we got good current flow (about 50 microamps) but did not short out or create an excessively high current. We did not, however, see (visually) good lead deposition. In the first experiments, no lead could be seen on our HOPG surface. However, by moving the counter/reference assembly even farther up the solution exit port, eventually we did get deposition, and were able to image the surface of the HOPG on which lead had been deposited using the fluid cell.

It should be noted that we still have not been able to image a sample while performing electrochemistry on it (that is, we have not seen the deposition occur while imaging). It seems that because of the relative placement of the counter/reference assembly, and the fact that deposition is only likely to occur on the part of the substrate closest to the counter electrode, it is unlikely that we will see deposition directly under the area scanned by our tip, and thus, we will be unable to see deposition happening in real time with the fluid cell in its current configuration.

Therefore, we will in future perform the deposition of a metal of choice and then image it subsequently.

Future experiments include finding the deposition parameters for Pt onto HOPG, and using the minicell to plate out Pt onto a nanostructure. Additionally, we will try to redesign the fluid cell so that it can be used as intended. Such a design should imitate the minicell in that the working-reference and working-counter electrode distances are the same. It should also use a counter electrode with a large surface-area exposed to the electrolyte, and one which is localized over the whole working electrode, so that deposition occurs smoothly and uniformly across the entire substrate surface.

References

1.J.N. Howard and C.A. Koval, "Design and Performance of a Minielectrochemical Cell for Spatial Resolution of 2-D Structures," Anal. Chem., in press.

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